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Thermodynamic properties of ferroelectric $NH_3CH_2COOH \cdot H_2PO_3$ crystal

I.R. Zachek[a], Ya. Shchur[b,*], R.R. Levitskii[b], A.S. Vdovych[b]

[a] *Lviv Polytechnic National University, 12 Bandery str., 79013 L'viv, Ukraine*
[b] *Institute for Condensed Matter Physics, 1 Svientsitskii str., 79011 L'viv, Ukraine*

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ABSTRACT

Using a modified microscopic model of $NH_3CH_2COOH \cdot H_2PO_3$ by taking into account piezoelectric coupling with strains ε_i, ε_4, ε_5 and ε_6 in two-particle cluster approximation, the temperature dependence of polarization and tensor of static dielectric permittivity of mechanically clamped and free crystal, their piezoelectric characteristics, elastic constants and heat capacity are calculated.

1. Introduction

Glycinium hydrogenphosphite crystal, $NH_3CH_2COOH \cdot H_2PO_3$ (GPI), is a very interesting compound due to the combination of structural elements typical of different classes of crystals. On the one hand, it contains the covalently bonded phosphite HPO_3 groups which are linked through the hydrogen $O - H \cdots O$ bonds thus forming the chains running approximately along the *c*-axis (see Fig. 1). Such structural components are usual for non-organic ferroelectric materials, in particular for crystals of KH_2PO_4 family. Exactly the hydrogen bonded PO_4 groups play a leading role in the mechanism of ferroelectric phase transition in KH_2PO_4-type crystals. On the other hand, there are four organic glycinium groups NH_3CH_2COOH in GPI unit cell which are linked by four additional hydrogen bonds with phosphite HPO_3 groups belonging to two different phosphite chains (see Fig. 1). Such a structural complexity may result in great diversity of physical properties of this material. Therefore, GPI crystal has been intensively studied by means of dielectric [1,2], acoustic [3–5], calorimetric [6], optic [7] and spectroscopic [8,9] methods. A theoretical description of dielectric properties of GPI was presented in [10,11].

At room temperature, GPI crystalizes in a monoclinic $P2_1/a$ space group (No. 14, Z = 4) which transforms to $P2_1$ symmetry (No. 4, Z = 4) [12–14] below structural phase transition occurring near $T_C = 224$ K. High-temperature phase is non-polar paraelectric phase whereas the low-temperature one demonstrates ferroelectric properties. Even at room temperature, there are two structurally inequivalent types of hydrogen bonds of different length, $O_2 - H_2 \cdots O_2$ (R = 2.48 Å) and $O_3 - H_3 \cdots O_3$ (R = 2.51 Å), phosphite HPO_3 groups linked into chains along *c*-axis [13]. In both cases, the protons located there are disordered above T_C over the two possible sites on hydrogen bonds whereas they become ordered in one of those sites below T_C. This proton ordering in low-symmetry phase is a common feature of many hydrogen bonded ferroelectrics. However, there is an unique feature distinguishing hydrogen bonds of GPI among other ferroelectics of order-disorder type. As seen in Fig. 1, every O_2 atom is involved only into a single $O_2 - H_2 \cdots O_2$ hydrogen bond whereas every O_3 atom is engaged into two different hydrogen bonds, i.e., $O_3 - H_3 \cdots O_3$ and $O_3 - H_6 \cdots N$. This additional hydrogen bond may puzzle the mechanism of phase transition. Based on the lattice dynamics simulation of GPI in both structural phases [15] it was established that mean square displacements of O_2 atoms in low-frequency range of 0–500 cm^{-1} are of one order of magnitude larger than those of O_3 atoms. However, the H_2 and H_3 protons have almost similar thermal vibration amplitudes over the frequency range, 0–1000 cm^{-1}.

Hence, an attempt to shed light onto the GPI phase transition mechanism is the main motivation for the present study. In our former works, we succeeded in the efforts to properly describe the set of thermodynamic, elastic and piezoelectric properties of hydrogen-

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[*] Corresponding author.
E-mail address: shchur@icmp.lviv.ua (Y. Shchur).

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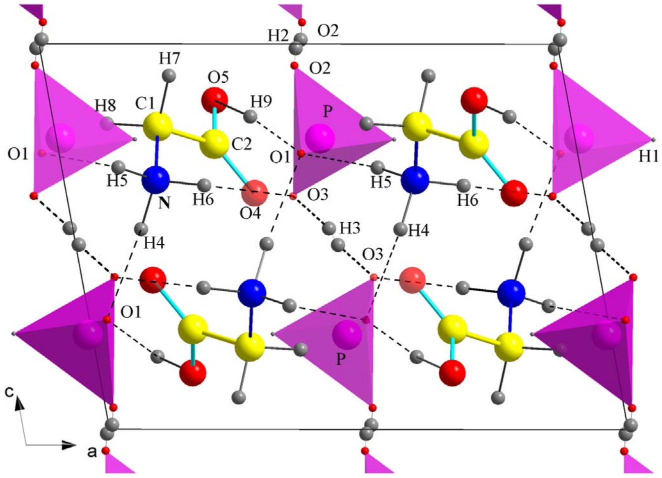

Fig. 1. Crystal structure of GPI in paraelectric phase.

bonded compounds with phase transitions of order-disorder type in the framework of pseudo-spin model for a proton subsystem within a two-particle cluster approximation [16,17]. In the present work, we are aiming at elaborating a pseudo-spin model of GPI crystal capable of describing the set of thermodynamic properties observed experimentally. Constructing such a model we took into consideration the ground structural feature occurring at the phase transition, namely proton ordering within $O_2 - H_2 \cdots O_2$ and $O_3 - H_3 \cdots O_3$ hydrogen bonds. All other structural changes are treated by us effectively using adjustable model parameters. If our description adequately correlates with experiment, especially within the phase transition region, it should count in favor of order-disorder mechanism of the ferroelectric phase transition in GPI.

2. Model Hamiltonian

We consider the system of protons, based on $O_2 - H_2 \cdots O_2$ and $O_3 - H_3 \cdots O_3$ bonds, which form zigzag chains along crystallographic *c*-axis. Dipole moments $\overrightarrow{d}_{qf}(f = 1, 3)$ are ascribed to two H_2 protons located on the neighboring chains along a-axis, whereas dipole moments $\overrightarrow{d}_{qf}(f = 2, 4)$ are related to two H_3 protons on the same neighboring chains (see Fig. 2). In ferroelectric phase, the dipole moments compensate each other ($\overrightarrow{d}_{q1}$ with $\overrightarrow{d}_{q3}$, $\overrightarrow{d}_{q2}$ with $\overrightarrow{d}_{q4}$) along Z and X directions (X ⊥(b,c), Y ||b, Z ||c). However, along Y axis, they have non-zero components contributing to the total spontaneous polarization.

Pseudo-spin variables $\frac{\sigma_{q1}}{2}, \ldots, \frac{\sigma_{q4}}{2}$ describe the changes related to reorientation of dipole moments of base units: $\overrightarrow{d}_{qf} = \mu_f \frac{\sigma_{qf}}{2}$. Mean values $\langle \frac{\sigma}{2} \rangle = \frac{1}{2}(n_a - n_b)$ imply the difference in occupancy of two possible proton positions on a hydrogen bond, n_a and n_b.

Hamiltonian of GPI proton may be presented as the sum of "seed" and pseudo-spin constituents. "Seed" energy U_{pseed} effectively accounts for the crystal lattice and does not directly depend on proton configurations. Pseudo-spin part of Hamiltonian considers short-range $\widehat{H}_{short}$ and long-range $\widehat{H}_{MF}$ proton interactions near tetrahedral HPO_3 groups and also takes into account the interaction with cartesian components of electric field E_1, E_2 and E_3. Therefore, Hamiltonian may be written as follows:

$$\widehat{H} = NU_{seed} + \widehat{H}_{short} + \widehat{H}_{MF} - \tag{2.1}$$

$$-E_1 \sum_q \left(\mu_{13}^x \frac{\sigma_{q1}}{2} - \mu_{24}^x \frac{\sigma_{q2}}{2} - \mu_{13}^x \frac{\sigma_{q3}}{2} + \mu_{24}^x \frac{\sigma_{q4}}{2} \right) -$$

$$-E_2 \sum_q \left(\mu_{13}^y \frac{\sigma_{q1}}{2} - \mu_{24}^y \frac{\sigma_{q2}}{2} + \mu_{13}^y \frac{\sigma_{q3}}{2} - \mu_{24}^y \frac{\sigma_{q4}}{2} \right) -$$

$$-E_3 \sum_q \left(\mu_{13}^z \frac{\sigma_{q1}}{2} + \mu_{24}^z \frac{\sigma_{q2}}{2} - \mu_{13}^z \frac{\sigma_{q3}}{2} - \mu_{24}^z \frac{\sigma_{q4}}{2} \right).$$

where v is unit cell volume, N is the total number of unit cells. In (2.1) $\mu_{13}^{x,y,z}$, $\mu_{24}^{x,y,z}$ are effective dipole moments per one pseudo-spin; σ_{qf} is y-component of pseudo-spin operator, which corresponds to the proton located in the q-th cell on the f-th bond ($f = 1, 2, 3, 4$).

"Seed" U_{seed} energy includes the elastic, piezolectric and dielectric constituents related to electric fields $E_i (i = 1, 2, 3)$ and strains ε_i and ε_j $(j = i + 3)$. $c_{jj}^{E0}(T)$, e_{ij}^0, $\chi_{ii}^{\varepsilon 0}$ correspond to the so-called "seed" elastic constants, piezoelectric stresses and dielectric susceptibilities, respectively:

$$U_{seed} = v \left(\frac{1}{2} \sum_{i,i'=1}^{3} c_{ii'}^{E0}(T) \varepsilon_i \varepsilon_{i'} + \frac{1}{2} \sum_{j=4}^{6} c_{jj}^{E0}(T) \varepsilon_j^2 + \sum_{i=1}^{3} c_{i5}^{E0}(T) \varepsilon_i \varepsilon_5 + c_{46}^{E0}(T) \right.$$

$$\varepsilon_4 \varepsilon_6 -$$

$$- \sum_{i=1}^{3} e_{2i}^0 \varepsilon_i E_2 - e_{25}^0 \varepsilon_5 E_2 - e_{14}^0 \varepsilon_4 E_1 - e_{16}^0 \varepsilon_6 E_1 - e_{34}^0 \varepsilon_4 E_3 - e_{36}^0 \varepsilon_6 E_3 - \tag{2.2}$$

$$\left. - \frac{1}{2} \chi_{11}^{\varepsilon 0} E_1^2 - \frac{1}{2} \chi_{22}^{\varepsilon 0} E_2^2 - \frac{1}{2} \chi_{33}^{\varepsilon 0} E_3^2 - \chi_{31}^{\varepsilon 0} E_3 E_1 \right).$$

Hamiltonian of short-range interactions has the following form

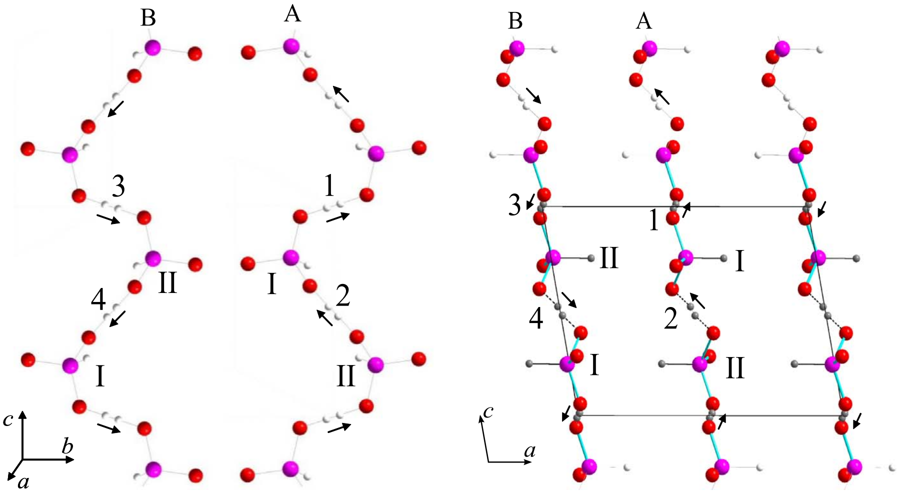

Fig. 2. Orientations of vectors $\mathbf{d}_{qf}$ in unit cell in ferroelectric phase.